

Appendix A

Equilibrium calculations

The interpretation of the carbothermic silicon process is, to a large degree, based on chemical equilibria, and a sound understanding of these equilibria is essential. This appendix presents the most important equilibrium calculations, reviews the available data sources, and warns against some common errors in the use of equilibrium calculations in the Si–O–C system.

Reactions in the submerged arc furnace

There are several approaches to the equilibrium evaluation of a system, and we will describe in detail one method that we think is both illustrative and convenient for the silicon process. In brief, we study the equilibria between the gas and the possible combinations of condensed phases. We write down a complete set of independent reactions for the possible phase combinations and derive the equilibrium relations from the mass action law. This procedure should provide a broad understanding of the equilibria of the furnace reactions in the silicon process.

Brief description of the system

The Si–O–C system has a gas phase and four condensed phases, SiO_2 , C, SiC and Si, in the temperature range 1400–2500°C where the main reactions take place. Species SiO_2 and Si have melting points within the temperature range of the reactions, and SiO_2 has several modifications. However, phase transformations within the species have no significant influence on the equilibria of the silicon process and will not be considered further. Any mutual solubility between the condensed phases is ignored. In the gas phase, the main species are CO and SiO, while several species occur in low concentrations: CO_2 , Si,

Si_2C , SiC_2 , etc. It has also been claimed that SiO can occur as a condensed species. It is disregarded in the calculations, but its existence will be discussed in connection with the data sources in Section A.2.

Calculation of equilibria

Motzfeldt gave one of the first interpretations of the silicon process based on equilibrium calculations (Motzfeldt, 1961). He calculated the vapour pressures for the possible combinations of condensed phases around the temperature of silicon formation and set up a crude process model based on the results. The numerical values of his pressure calculations are misleading because the thermochemical data then available were incorrect, but his general approach to the problem will be used here with more recent data (Chase *et al.*, 1985). He used a graphical treatment that gives a very good sense of the chemistry of the system, but numerical calculation on a computer is much faster and gives better accuracy than measurements on a graph. Here, the problem will be approached, and the results will be presented, as in a graphical method, but all the calculations have been carried out on a computer.

In a two-dimensional diagram, it is possible to represent system properties as a function of one independent variable. The conditions for unambiguous specification are given by the phase rule for the system. Generally, a system may consist of a number C of components and have a number Ph of phases. At equilibrium, it has a restricted number F of free variables, or ‘degrees of freedom’. According to Gibbs’ phase rule, we then have

$$Ph + F = C + 2 \quad [\text{A.1}]$$

Determining the correct number of components, C , sometimes causes difficulties, but in high-temperature systems with reduction/oxidation reactions it is safe to take C as the number of elements. Thus, in the present case $C = 3$ (Si, O, C), and we have

$$Ph + F = 5 \quad [\text{A.2}]$$

In systems without reduction/oxidation reactions, C may be lower than the number of elements. An example is the slag system $\text{SiO}_2\text{--CaO}$, which has only

two components even if there are three elements. Rigid rules for determining the number of components can be found in standard texts of thermodynamics.

When we present an equilibrium as a two-dimensional graph, we need one degree of freedom for the independent variable. The sum of phases and fixed variables must therefore be four to determine the dependent variables unambiguously for a given value of the independent variable. The thermodynamic variables considered are temperature, pressure and chemical composition of the phases. The chemical composition of the gas phase is given as the partial pressure. In equilibrium calculations, all reactions are equally correct if they are balanced and the system is completely determined according to the phase rule. It does not matter whether a reaction really occurs. The selection of reactions for the calculation is therefore mainly a matter of convenience. The result is the same for all correct combinations of reactions in the calculation.

The calculations are based upon the constant K in the mass action law. This constant for a Reaction $[x]$ can be calculated by the equation

$$\ln K_x = \frac{-\Delta G_x^0}{RT} \quad [\text{A.3}]$$

where ΔG_x^0 is the difference in standard Gibbs energy between the right- and left-hand sides of the Reaction $[x]$, R is the gas constant $8.314 \text{ J/K}^{-1}\text{mol}^{-1}$, and T is the temperature in K. The K_x values are, as a rule, calculated from (Chase *et al.*, 1985). We assume that the gases in all systems are ideal and use the partial pressures directly in the mass action law. The partial pressure p in equilibrium calculations is a relative pressure, defined as the ratio between the actual pressure and the pressure in the standard state of the thermochemical data. It is therefore really a dimensionless number, but the unit (bar) is normally added to indicate that the standard state is 1 bar.

The calculation will be shown in several examples later. Generally, it starts with a system that is completely determined according to the phase rule. Then, as a first approximation, it is assumed that CO and SiO are the only gas species in the system. The mass action law equations are correct even if there are other gas species present, and the approximation is introduced in the equation that relates the partial pressures to the ambient pressure P_{amb} .

$$p_{\text{SiO}} + p_{\text{CO}} = p_s = P_{amb} - p_x \quad [\text{A.4}]$$

where p_s is defined by the equation, P_{amb} is the pressure of the surroundings (normally 1 bar for a silicon furnace), and p_x is the sum of the partial pressures of all other gases in the system. The first approximation $p_s = P_{amb} = 1$ bar gives approximate SiO and CO pressures. To introduce other gas species, an additional mass action equation with the new species must be added. The calculation of the partial pressure of CO_2 will be shown as an example. The additional mass action equation can be based on any reaction between CO_2 and the other species, and we select one that is convenient for the calculation, such as



with the mass action equation

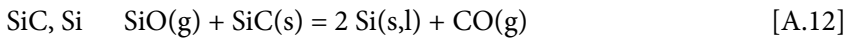
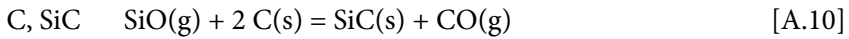
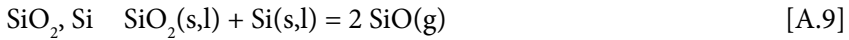
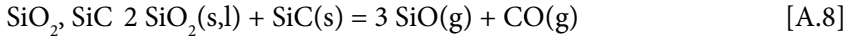
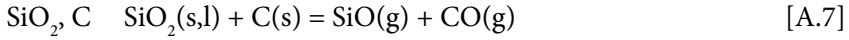
$$\frac{p_{\text{SiO}} \cdot p_{\text{CO}_2}}{p_{\text{CO}}} = K_{\text{A.5}} \text{ that is } p_{\text{CO}_2} = K_{\text{A.5}} \cdot \frac{p_{\text{CO}}}{p_{\text{SiO}}} \quad [\text{A.6}]$$

The approximate partial pressures of SiO and CO are known from the first approximation. The CO_2 partial pressure can provide an improved p_s by Equation [A.4], and then new partial pressures of SiO and CO, which in turn can give an improved partial pressure of CO_2 . This iteration can be repeated until the sum of the partial pressures is equal to the ambient pressure with sufficient accuracy. Other gas species such as Si, Si_2 , SiC_2 , Si_2C , etc. can be included in the calculation simultaneously by analogous reactions. Calculations for the conditions in silicon furnaces show that, for most purposes, it is sufficient to assume that SiO and CO are the only gas species.

Equilibria with two condensed phases

A gas phase is always present in the furnace reactions. For two condensed phases, the phase rule then gives two degrees of freedom. One is used for the free variable; one additional property then has to be fixed to determine the dependent variable completely. The equilibrium can therefore be determined at *constant temperature* or *constant pressure*.

The system has a total of four condensed phases in the interesting temperature range: SiO_2 , C, SiC and Si. There are six combinations of two condensed phases, and these combinations can be expressed as chemical reactions:



Reaction [A.11] is metastable because Si will react with C at all relevant temperatures until either Si or C is consumed:



The condensed phases are then either C–SiC or Si–SiC, and the corresponding reactions are Reactions [A.10] and [A.12], respectively.

Constant temperature

At constant temperature, two condensed phases and one partial pressure specify the system completely according to the phase rule. We choose the CO pressure as the independent variable and show the SiO pressure as the dependent variable. The equilibrium Reactions [A.7]–[A.12] give mass action laws, written here in logarithmic form for reasons that will be explained later:

$$\lg p_{\text{CO}} + \lg p_{\text{SiO}} = \lg K_{\text{A.7}} \quad [\text{A.14}]$$

$$\lg p_{\text{CO}} + 3 \lg p_{\text{SiO}} = \lg K_{\text{A.8}} \quad [\text{A.15}]$$

$$2 \lg p_{\text{SiO}} = \lg K_{\text{A.9}} \quad [\text{A.16}]$$

$$\lg p_{\text{CO}} - \lg p_{\text{SiO}} = \lg K_{\text{A.10}} \quad [\text{A.17}]$$

$$\lg p_{\text{CO}} - \lg p_{\text{SiO}} = \lg K_{\text{A.11}} \quad [\text{A.18}]$$

$$\lg p_{\text{CO}} - \lg p_{\text{SiO}} = \lg K_{\text{A.12}} \quad [\text{A.19}]$$

When T is constant, Equations [A.14]–[A.19] give straight lines in a graph of $\lg p_{\text{SiO}}$ as a function of $\lg p_{\text{CO}}$. This linear relation is why the mass action equations are written in logarithmic form. An example of equilibrium is shown in Figure A.1, and changes with temperature are indicated in Figure A.2. The directions of the lines are determined by the stoichiometry of the equations; temperature affects only the magnitude of the equilibrium constant K_x . When temperature changes, a line is displaced parallel to the original line. With increasing temperature, the stability ranges for C and SiC come closer. Figure A.2 can be interpreted as the projection of a three-dimensional graph of the SiO pressure as a function of the CO pressure and the temperature.

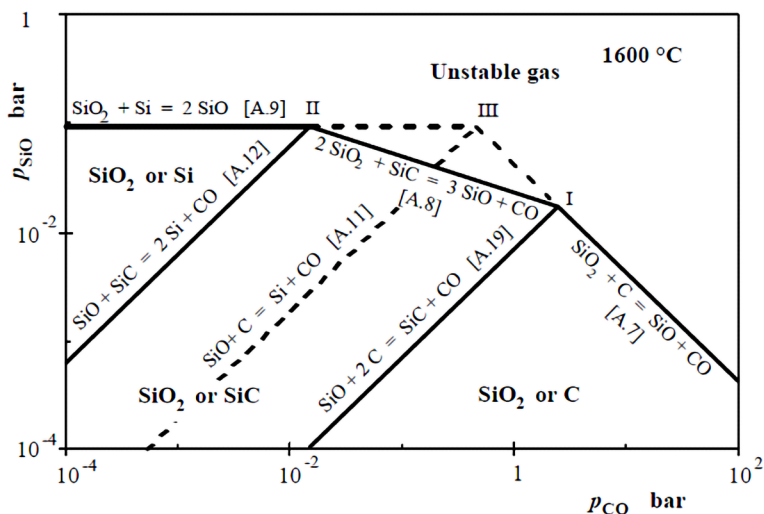


Figure A.1 Vapour pressures at constant temperature 1600°C of reactions with two condensed phases in the system Si–O–C. The broken lines represent metastable equilibria.

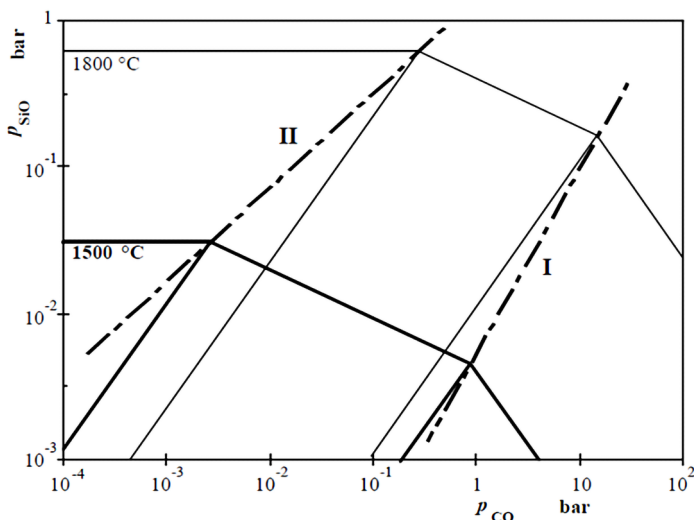


Figure A.2 The displacement with temperature of the vapour pressure graphs shown in Figure A.1.

The graphs split the area of Figure A.1 into stability zones. As an example, we consider the reaction



For gas compositions corresponding to points above the graph, the product $p_{\text{SiO}} \cdot p_{\text{CO}}$ is larger than the equilibrium value in the mass action law. If SiO and CO are removed in the ratio given by the stoichiometry of the reaction, the product $p_{\text{SiO}} \cdot p_{\text{CO}}$ moves towards the equilibrium value. Therefore, in Reaction [A.7] the gas is unstable. Analogous arguments apply to Reactions [A.8] and [A.9], and the three reactions together define the zone Unstable gas in Figure A.1. Gas mixtures corresponding to points in this area cannot exist at equilibrium.

In the area between the graphs, one condensed phase is allowed. The phase SiO_2 is stable for all stable gas compositions, since there are no reactions between it and the gas species SiO and CO that can form the other condensed species. Therefore, the stable condensed phase in an area will be SiO_2 or one of the phases C, SiC and Si. The condensed phases other than SiO_2 have stability areas that can be found by discussing the chemical reactions.

As an example, we discuss the stability range of Si. Si is stable for SiO pressures higher than the equilibrium value of



In the diagram, Si is stable above the graph of Reaction [A.12]; below the graph it becomes unstable relative to SiC. However, above the graph of



the gas is unstable. Therefore, Si is stable only between the graphs of Reactions [A.9] and [A.12], to the left of the intersection. The stability ranges of SiC and C can be discussed similarly. The complete stability distribution is indicated in Figure A.1. The metastable system shown by broken lines is ignored in the stability discussion.

Constant pressure

At constant pressure, two condensed phases and the temperature specify the system completely according to Equation [A.1]. Therefore, the SiO pressure can be presented in a graph as a function of temperature. Such graphs will be calculated for equilibria of Reactions [A.7]–[A.12]. The partial pressures must obey the mass action equations of the reactions, and their sum must equal the ambient pressure.

For Reaction [A.7] we have the mass action reaction

$$p_{\text{SiO}} \cdot p_{\text{CO}} = K_{\text{A.7}} \quad [\text{A.20}]$$

together with

$$p_{\text{SiO}} + p_{\text{CO}} = P_{\text{amb}} - p_x = p_s \quad [\text{A.4}]$$

where p_x symbolizes the sum of the other gas species in the system (CO_2 , Si, Si_2 , SiC_2 , Si_2C , ...), and p_s is the sum $p_{\text{SiO}} + p_{\text{CO}}$ corrected for the other gas species. The pressures of these gas species can be calculated as indicated above in connection with Equation [A.4]. Equations [A.20] and [A.4] combine to

$$p_{\text{SiO}}^2 - p_s \cdot p_{\text{SiO}} + K_{\text{A.7}} = 0 \quad [\text{A.21}]$$

The solution of this equation can be taken as the intersection between the curves

$$y_1 = p_{\text{SiO}}^2 - p_s \cdot p_{\text{SiO}} + K_{\text{A.7}} \text{ and} \quad [\text{A.22}]$$

$$y_2 = 0 \quad [\text{A.23}]$$

Equation [A.22] gives

$$\frac{dy_1}{dp_{\text{SiO}}} = 2 \cdot p_{\text{SiO}} - p_s$$

$$\frac{d^2 y_1}{dp_{\text{SiO}}^2} = 2$$

The variable y_1 has a minimum for $p_{\text{SiO}} = 0.5 p_s$. The graphs for y_1 and y_2 have two intersections if

$$y_{1,\min} = 0.25 p_s^2 - 0.5 p_s^2 + K_{\text{A.7}} = K_{\text{A.7}} - 0.25 p_s^2 < 0$$

and one intersection with $p_{\text{SiO}} = 0.5 p_s$ if $y_{1,\min} = 0$. If $y_{1,\min}$ is higher, the graphs do not intersect, which means that Equation [A.22] has no real solutions. In the range with two solutions, one is larger and one is smaller than 0.5. The condition for a solution is

$$p_s \geq 2 \cdot \sqrt{K_{\text{A.7}}} \quad (p_s \text{ and } K_{\text{A.7}} \text{ are always positive}) \quad [\text{A.24}]$$

Equation [A.22] can be solved analytically:

$$p_{\text{SiO}} = 0.5 p_s \pm \sqrt{0.25 p_s^2 - K_{\text{A.7}}} \quad [\text{A.25}]$$

The solution is shown in Figure A.3. The stoichiometry of the reaction



does not allow solutions with $p_{\text{SiO}} > 0.5$ from the reactants SiO_2 and C, and establishing this equilibrium will require an external source of SiO. As can be seen from Figure A.3, the high SiO pressures are unstable relative to

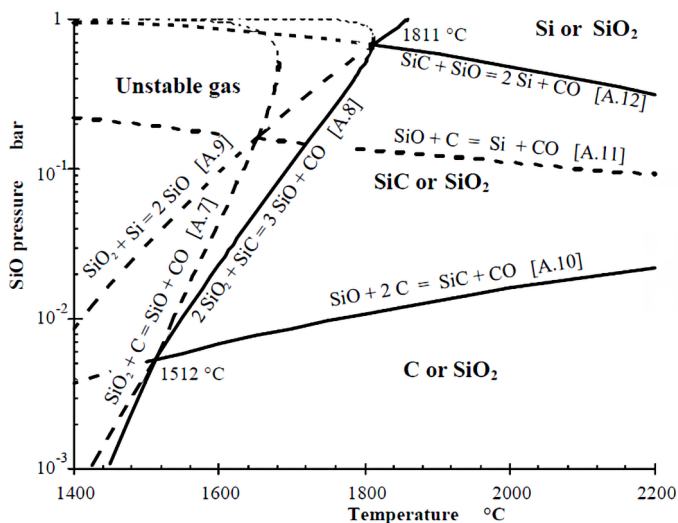


Figure A.3 *Equilibrium SiO pressures above the condensed phase combinations C–SiC, C–Si, SiO₂–C, SiO₂–SiC, SiC–Si and SiO₂–Si calculated with data from the JANAF Thermochemical Tables (Chase, 1985). The broken lines indicate metastable equilibria.*

Similarly, Reaction [A.8] gives an equation

$$p_{\text{SiO}}^4 - p_S p_{\text{SiO}}^3 + K_{A.8} = 0 \quad [\text{A.26}]$$

A discussion similar to that for Reaction [A.7] shows that the equation has two solutions for

$$y_{1,min} = K_{A.8} - 0.1055 p_s^4 < 0 \quad [A.27]$$

and one solution for $y_{1,min} = 0$. The equation has real solutions if

$$p_s \geq 1.755 \cdot \sqrt[4]{K_{A.8}} \quad [A.28]$$

It can be solved by 'trial and error' or by a systematic iteration method, e.g. by Newton iteration. The graph is included in Figure A.3. The stoichiometry does not allow solutions with $p_{\text{SiO}} > 0.75$ from the reactants SiO_2 and SiC .

The SiO pressure of Reaction [A.9] is independent of the presence of other gases:

$$p_{\text{SiO}} = \sqrt{K_{A.9}} \quad [A.29]$$

Reactions [A.10], [A.11] and [A.12] have similar mass action equations; only the value of the equilibrium constant K_x is different.

$$\frac{p_{\text{CO}}}{p_{\text{SiO}}} = K_x \quad [A.30]$$

$$p_{\text{SiO}} + p_{\text{CO}} = p_s \quad [A.20]$$

The solution is

$$p_{\text{SiO}} = \frac{p_s}{K_x + 1} \quad [A.31]$$

The areas between the graphs in Figure A.3 do not uniquely define which condensed phase is stable. Gas compositions to the left of one of Reactions [A.7], [A.8] and [A.9] are unstable with respect to condensation, and the reactions together define the area Unstable gas as in Figure A.1. The stability of condensed phases between the graphs can be discussed analogously to Figure A.1, and the resulting stable phases are shown in the figure. The stability zones are not important, since the graphs will be used mainly in discussing situations where two or three condensed phases are present.

Equilibria with three condensed phases

Figure A.1 shows which condensed phases can coexist in equilibrium. At the intersection of the lines in Figure A.1, there are three condensed species, and the gas composition is fixed for the given temperature. There are three intersections:

I Condensed phases: SiO_2 , C, SiC

II Condensed phases: SiO_2 , SiC, Si

III Condensed phases: SiO_2 , C, Si metastable

In addition, there is a fourth combination of three phases:

IV Condensed phases: C, SiC, Si metastable

Combination IV does not appear in a CO–SiO diagram. It is metastable and uninteresting for a production process because it does not include the silicon source SiO_2 . It will not be discussed further.

The pressures of CO and SiO can be calculated directly by combining the reactions that give the intersections. Figure A.1 gives three reactions for each intersection, and the most convenient reactions for calculation are chosen.

Point of intersection I: Combining Reactions [A.7] and [A.10]:

$$p_{\text{SiO}} = \sqrt{K_{4.7} / K_{A.10}} \quad [\text{A.32}]$$

$$p_{\text{CO}} = \sqrt{K_{4.7} \cdot K_{A.10}} \quad [\text{A.33}]$$

Point of intersection II: Combining Reactions [A.9] and [A.12]:

$$p_{\text{SiO}} = \sqrt{K_{A.9}} \quad [\text{A.29}]$$

$$p_{\text{CO}} = \sqrt{K_{A.9}} \cdot K_{A.12} \quad [\text{A.34}]$$

Point of intersection III: Combining Reactions [A.9] and [A.11]:

$$p_{\text{SiO}} = \sqrt{K_{A.9}} \quad [\text{A.29}]$$

$$p_{\text{CO}} = \sqrt{K_{A.9}} \cdot K_{A.11} \quad [\text{A.35}]$$

This combination is metastable and will not be discussed further.

The gas pressure in phase combination I (SiO_2 –C–SiC) is shown in Figure 2.7, and the pressure in phase combination II (SiO_2 –SiC–Si) in Figure 2.8.

Equilibrium with four condensed phases

SiO_2 , C, SiC and Si can, in principle, coexist and give a completely determined system. In an extension of Figure A.2, the system can be found as the intersection of graphs I and II. With increasing temperature, the graphs move closer and closer together. Numerical calculation shows that they are still apart at 2700°C. At approximately this temperature, SiC dissociates to C and a Si phase with a high content of carbon. The assumptions for the calculation of a four-phase equilibrium then break down. It can be concluded that equilibrium among the four condensed phases SiO_2 , C, SiC and Si corresponds to very high temperature and pressure. Most likely, it cannot be realized because SiC dissociates at a lower temperature. In any case, it lies outside the interesting temperature range of the silicon process.

The data sources

Thermochemical data for the Si–O–C system are available in FactSage and HSC Chemistry. In the first version of this book (1998), they were taken from JANAF Thermochemical Tables (Bahrin, 1995; Bahrin *et al.*, 1977; Bahrin and Knacke, 1973; Chase *et al.*, 1985; Knacke and Kubaschewski, 1991; Kubaschewski *et al.*, 1993). Differences between the sources account for temperature differences of about 20 K. The data were compiled from measurements with scatter and were sometimes extrapolated outside the experimental range. Therefore, they always have a rather large uncertainty, and the results should be interpreted with care. When reaction temperatures are calculated, the result is not reliable to the nearest °C. Still, there is no reason to expect that improved accuracy of the data will give a qualitative change in process understanding.

Most printed data sources give tables with values for each 100 K, as well as additional values for transition points such as melting, vaporization and transformations of the crystalline structure. For computer calculations, it would be more convenient to store the data in a form where the value for any given temperature could be retrieved directly. With the present availability of fairly high-powered personal computers, there is really no need for tables. Kubaschewski *et al.* have a formula system for tabulation of thermochemical data in formula form, but calculation of ΔG° data from these tables is still rather time-consuming (Kubaschewski *et al.*, 1993). Programmes for thermochemical

calculations (e.g. HSC Chemistry) contain extensive data compilations with information about the data sources. Without access to suitable programmes, one can use tables and obtain fairly high accuracy by interpolating linearly between the given temperatures.

Thermochemical calculations from about 1965 and earlier are based on incorrect data. The reason was an erroneous measurement of the heat of formation for SiO_2 . These data gave inconsistent results in thermodynamic analysis. Chipman showed that the inconsistencies disappeared if the heat of formation of SiO_2 was changed (Chipman, 1961). Later, new measurements showed that Chipman's indications were correct, and revised data were included in the thermochemical tables. The consequence of the correction for the Si–O–C system is discussed in (Schei, 1967; Schei and Sandberg, 1966).

In the data sources used here, SiO is not included as a stable condensed material, most likely because the compilers found no convincing experimental demonstration of its existence. Kubaschewski *et al.* (1993, reprinted from earlier editions of the book) give an example where the thermochemical properties of condensed (amorphous) SiO are assessed tentatively, but they do not include it in their compilation of data. Still, Nagamori *et al.* used these tentative data as background for a new interpretation of the silicon process (Nagamori *et al.*, 1986). They calculated the equilibrium for the reaction when $[\text{SiO}_2 + x \text{ SiC}]$ is heated, and found that the reactants will gasify without Si formation according to



Therefore, they concluded that Si cannot be produced in an isothermal reaction in this system. When they introduced condensed SiO into the calculation with the tentative data of Kubaschewski, the SiO(cond)–SiC–Si system at 1 bar gave Si. Therefore, in their opinion, condensed SiO is an essential intermediate in the reaction between SiO_2 and C or SiC. Rosenqvist and Tuset pointed out that there is no reliable evidence for the existence of SiO(l) and claimed that existing metallurgical theory explains the silicon process satisfactorily (Rosenqvist and Tuset, 1987). However, Nagamori *et al.* (1987) repeated their claims that Si production would be impossible without condensed SiO.

The reasoning of Nagamori *et al.* (1986) was based on a calculation indicating vaporization without Si formation when mixtures $[\text{SiO}_2 + x \text{ SiC}]$ are

heated. This result differs from the calculation in Chapter 2 and several similar published calculations. The reason for the difference is that Nagamori *et al.* (1986) used the approximate data of Turkdogan instead of Turkdogan's source, which is an earlier edition of the JANAF Thermochemical Tables (this edition gives essentially the same data as the later edition for the relevant species) (Chase *et al.*, 1985; Turkdogan, 1980). In the paper of Nagamori *et al.* (1986), the calculated temperature in the inner zone of the furnace increases when condensed SiO is introduced, because a higher temperature becomes necessary to obtain an overall pressure of 1 bar. This higher temperature gives a more favorable ratio $p_{\text{CO}}/p_{\text{SiO}}$ for silicon formation. However, direct measurements of the SiO_2 -SiC-Si system give a total vapour pressure fairly close to the values calculated from the JANAF data (Gjerstad, 1968). If condensed SiO really is formed in the furnace, it should also have been present in the measurements; these measurements must then be valid for the SiO(cond)-SiC-Si system. Therefore, the temperatures and SiO content calculated in Chapter 2 should be qualitatively correct, whether condensed SiO is stable or not. The existence of condensed SiO is not relevant for estimation of the temperature in the furnace, and the paper of Nagamori *et al.* does not corroborate its existence (Nagamori *et al.*, 1987).

Common errors in equilibrium calculations

The literature shows some errors in equilibrium calculations for the silicon process. In this Section, we present some examples of common errors as a warning. However, apparently erroneous calculations are not always mistakes. In some cases, one can simulate kinetics by applying equilibrium calculations in systems that are only semistable. For example, in the cooling of the gas mixture SiO and CO, we know from experience that the product is $\text{SiO}_2(\text{s,l})$ and Si(l), while equilibrium results in Figure A.3 indicate $\text{SiO}_2(\text{s,l})$ and SiC(s) or C(s). This experience shows that the equilibrium reactions are slow, and we can simulate the real situation by calculating the semistable reaction.



Loss of accuracy by data treatment

High-temperature thermochemical data always have rather high error limits, but uncertainty should not be increased by mathematical treatment. Personal computers and calculation programmes with data are now widely available, and there is no reason to use strong simplifications, such as the one proposed by Turkdogan (1980). In this simplification, the Gibbs energy of formation is expressed as

$$\Delta_f G^\circ = A + B T \quad [\text{A.36}]$$

where A and B are constants over a given temperature range. This approach will cause problems with phase transitions. An example of a mistake caused by this error is the above-mentioned new interpretation of the silicon process by Nagamori *et al.* (1986, 1987).

Combination of species that cannot coexist

If we write the reaction



we can calculate values of $K_{\text{A.37}}$ for the requested temperatures. However, the result is not meaningful, because the species C and Si cannot coexist. This impossibility can be seen from the Gibbs energy of the reaction



which is negative over the interesting temperature range (Table A.1). This error can be avoided if we set up a phase stability diagram (also called a predominance diagram). The diagrams in Figures A.1–A.3 are examples of phase stability diagrams that show which phases can coexist. Si cannot be formed in a reaction between SiO_2 and C before all the C is consumed, and the real equilibrium reaction will be a combination of the following reactions:



However, the SiO content in the resulting gas will be low, and Reaction [A.38] is a good approximation of the real reaction.

Table A.1 *The standard Gibbs energy of Reaction [A.13] calculated by HSC Chemistry.*

Temperature °C	0	500	1000	1500	2000
ΔG° [A.13] kJ	-71.05	-67.24	-63.80	-57.66	-39.36

Ignoring important species

Another interpretation of the error of equilibrium calculations based on Reaction [A.37] is that we have ignored the important species SiC and SiO. Ignoring important species is especially dangerous if we carry out equilibrium calculations by minimization of the free energy. In that case, the programme varies the contents of the species that are included and reports the combination that gives the lowest free energy. This result may, however, be misleading, since the ignored species could have given a lower free energy.

Inattention to the phase rule

The reaction system of Reaction [A.37] has three condensed phases, and at fixed ambient pressure it has no degrees of freedom according to the phase rule. We can calculate the equilibrium constant for any temperature by ordinary methods and derive an equation for the partial pressure of CO as a function of temperature. However, since the system has no degrees of freedom, the temperature is determined by the system, and the calculated partial pressure is correct only at this temperature. We can use the equation together with another equation to determine the equilibrium temperature, but not to find the partial pressure of CO at an arbitrary temperature.

Unsuitable interpretation of the reaction conditions

If we want to find the partial pressure over SiO₂ and SiC at constant ambient pressure 1 bar, we can use the reaction



combined with a relation between partial and total pressure. The condition must be

$$p_{\text{SiO}} + p_{\text{CO}} = 1 \quad [\text{A.39}]$$

and not

$$p_{\text{SiO}} = 3 p_{\text{CO}} \quad [\text{A.40}]$$

The condition [A.40] is correct if the total pressure is not specified and the resulting gas combination is stable.

Another example may be the estimation of the equilibrium when a mixture $[\text{SiO}_2 + 2 \text{ C}]$ is heated at 1 bar to a temperature slightly above the triple point at 1811°C (Figure A.3). We assume that the sample is placed in a crucible with a small opening and heated. The criterion for reaction is then

$$p_{\text{total}} \approx p_{\text{SiO}} + p_{\text{CO}} = P_{\text{amb}} = 1 \text{ bar}$$

This criterion, which is really based on kinetic reasoning, is discussed in detail in Chapter 2. It gives a reaction sequence:

- Slow reaction to the triple point at 1512°C
- Formation of SiC until the C is consumed slightly above 1512°C, gas CO–SiO with a small content of SiO given off
- Slow reaction between SiO_2 and SiC to the triple point at 1811°C
- Formation of Si slightly above 1811°C until the SiO_2 is consumed, gas CO–SiO with a high content of SiO given off.

This reaction sequence gives a certain overall reaction. If we calculate the equilibrium for the mixture $[\text{SiO}_2 + x \text{ C}]$ directly at temperature 1811°C, by means such as the minimization of the free energy, we will get a different overall reaction. The reason is that the open crucible gives off CO to the surroundings slightly above 1512°C, and this CO is not present in the reaction at 1811°C in the reaction sequence. As a result, the reaction at 1811°C will have a higher SiO content in the sequential reaction than in the direct reaction, and the more favorable ratio $p_{\text{CO}}/p_{\text{SiO}}$ gives a higher Si yield.

Erroneous use of 'The reaction goes to the right for $\Delta G^\circ < 0$ '

The rule is always correct for phase combinations where no phase is a mixture. The reaction



is a good example. If ΔG° is negative, the reaction will go to the right until at least one of the phases Si or C is consumed. However, when at least one of the phases is a mixture, $\Delta G^\circ = 0$ only means that K has the value 1. For a gas producing reaction, the rule is true if the gas is a pure species and the ambient pressure is 1 bar. This condition is approximately fulfilled for the reaction



and the rule is a good approximation. For a more complex reaction, such as



$\Delta G_{\text{A.12}}^\circ$ gives

$$\frac{a_{\text{Si}}^2 \cdot p_{\text{Co}}}{p_{\text{SiO}}} = 1$$

When the product is pure silicon, the direction of the reaction depends on the gas pressure ratio. If the silicon phase is an alloy, a low Si activity can contribute strongly to drive the reaction to the right.

References

- Bahrin, I. (1995) *Thermochemical data of pure substances*. 3rd edn. Wiley-VCH. Available at: <https://doi.org/10.1002/9783527619825>
- Bahrin, I. and Knacke, O. (1973) *Thermochemical properties of inorganic substances*. 1st edn. Springer-Verlag Stahleisen.
- Bahrin, I., Knacke, O. and Kubaschewski, O. (1977) *Thermochemical properties of inorganic substances: Supplement*. 1st edn. Springer-Verlag Stahleisen.
- Chase, M.V. Jr., Davies, C.A., Downey, J.R. Jr., Frurip, D.J., MacDonald, R.A. and Syverud, A. (1985) *NIST-JANAF Thermochemical Tables*. Available at: <https://janaf.nist.gov/janbanr.html> (Accessed: 22 May 2025).
- Chipman, J. (1961) 'The free energy of silica', *J. Am. Chem. Soc.*, 83, pp. 1762–1763.
- Gjerstad, S. (1968) *Chemical metallurgical investigations concerning carbothermic reduction of alumina and silica*. Doctoral thesis. Norges Tekniske Høgskole (NTH), now Norwegian University of Science and Technology (NTNU).
- Knacke, O. and Kubaschewski, O. (1991) *Thermochemical properties of inorganic substances*. 2nd edn. Springer-Verlag Stahleisen.
- Kubaschewski, O., Alcock, C.B. and Spencer, P.J. (1993) *Materials thermochemistry*. 6th edn. Pergamon Press.
- Motzfeldt, K. (1961) *An evaluation of the chemistry of the ferrosilicon process, with the special aim of increasing the silicon recovery*. Report for Elkem, in Norwegian. Institute of Silicate Science at Norges Tekniske Høgskole (NTH), now Norwegian University of Science and Technology (NTNU), Trondheim, Norway.
- Nagamori, M., Malinsky, I. and Claveau, A. (1986) 'Thermodynamics of the Si–C–O system for the production of silicon carbide and metallic silicon', *Metallurgical Transactions B*, 17, pp. 503–514. Available at: <https://doi.org/10.1007/BF02670216>
- Nagamori, M., Malinsky, I. and Claveau, A. (1987) 'The role of SiO(l) in the production of metallic silicon. Authors' reply to a discussion contribution by Rosenqvist and Tuset (1987)', *Metallurgical Transactions B*, 18, pp. 472–477.
- Roine, A. (1997) *HSC Chemistry for Windows v. 9*. Outotec Research, Pori, Finland.
- Rosenqvist, T. and Tuset, J.K. (1987) 'Discussion of "Thermodynamics of the Si–O–C system for the production of silicon carbide and metallic silicon" (see Nagamori *et al.*, 1986)', *Metallurgical Transactions B*, 18B, pp. 471–472; authors' reply pp. 472–477.
- Schei, A. (1967) 'On the chemistry of ferrosilicon production', *Kjemi Bergvesen*, 27, pp. 152–158.
- Schei, A. and Sandberg, O. (1966) 'Back reactions during production of silicon metal in a submerged arc electric furnace', in *Scandinavian University Books*. Oslo: Universitetsforlaget, pp. 141–150.
- Turkdogan, E.T. (1980) *Physical chemistry of high temperature technology*. New York: Academic Press.